Heteropolyacids in PEM Fuel Cell Membranes for Higher Temperature Operation.

Andrew M. Herring and John A. Turner

Department of Chemical Engineering
Colorado School of Mines

Hydrogen and Electricity, Systems and Infrastructure Group
National Renewable Energy Laboratory

Golden, CO 80401

Collaboration

- Colorado School of Mines, CSM. (Engineering and Applied Science University)
  - Chemical Engineering
  - Applied Chemistry
  - Synthetic Inorganic Chemistry
  - NMR
- National Renewable Energy Laboratory, NREL.
  - Electro-Chemistry
  - Polymer Science

Interest in HPA

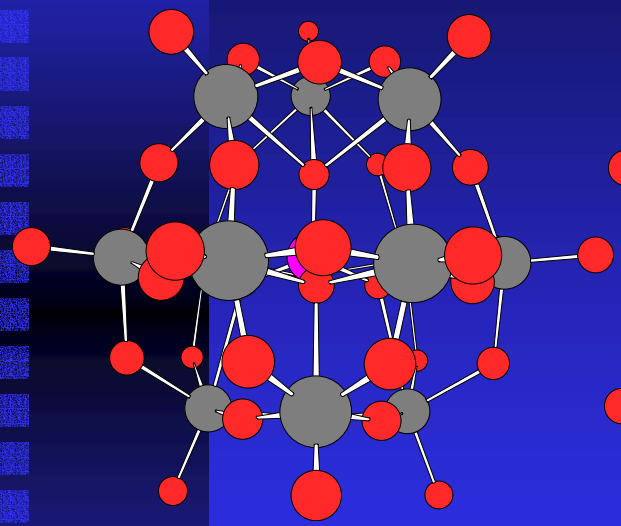
- Growing interest in HPA since early 1990s for enhancing PEM, especially at higher temperatures
- Most reports concern the 4 or 5 commercially available HPA (all of which are Keggin anions)
- Almost all reports involve adding HPA to existing systems as membrane extenders

- Very little on other members of this huge class of materials and no systematic study of structure/activity
- Few reports on HPA as the sole proton conducting functionality

Outline of Research

- Fundamental Study of H^+ Conduction in Inorganic Solids
- HPA/Perfluoropolymer Blends
- HPA Doped Nafion
- Sol Gel Membranes
- Hybrid HPA

Heteropoly Anions – Primary Structure



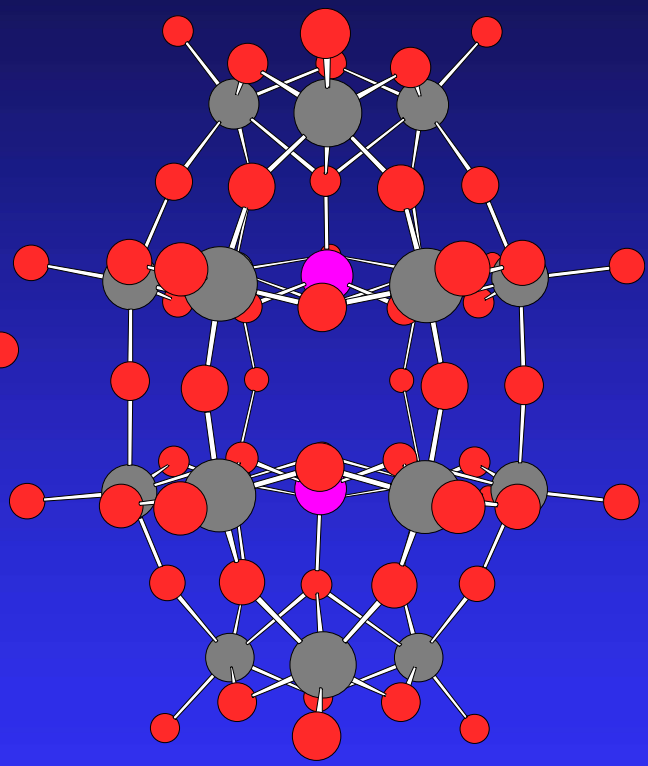
Keggin

$[PW_{12}O_{40}]^{3-}$ (HPW)

$[SiW_{12}O_{40}]^{4-}$ (HSiW)

$[ZnW_{12}O_{40}]^{6-}$ (HZnW)

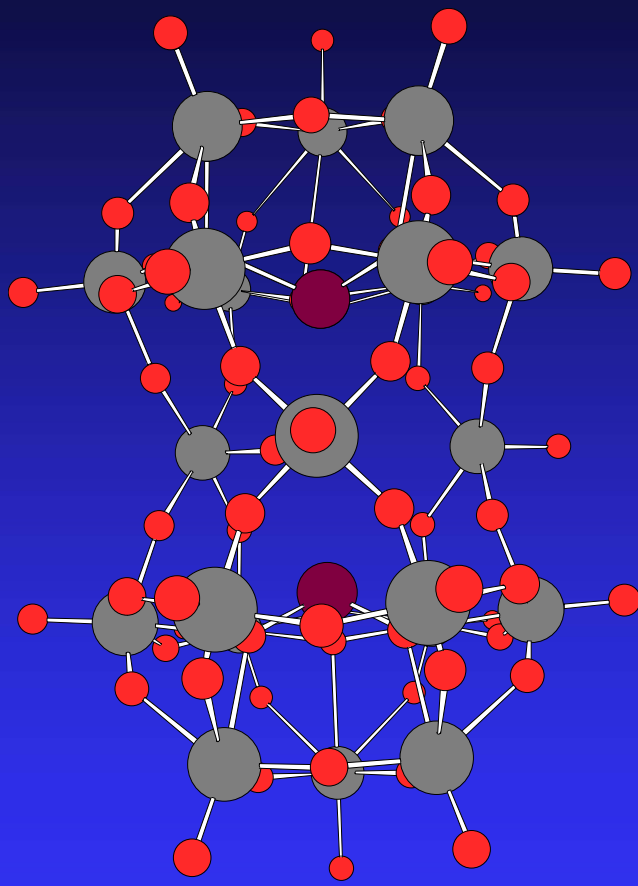
$[CoW_{12}O_{40}]^{6-}$ (HCoW)



Dawson

$[P_2W_{18}O_{62}]^{6-}$

(HP2W)



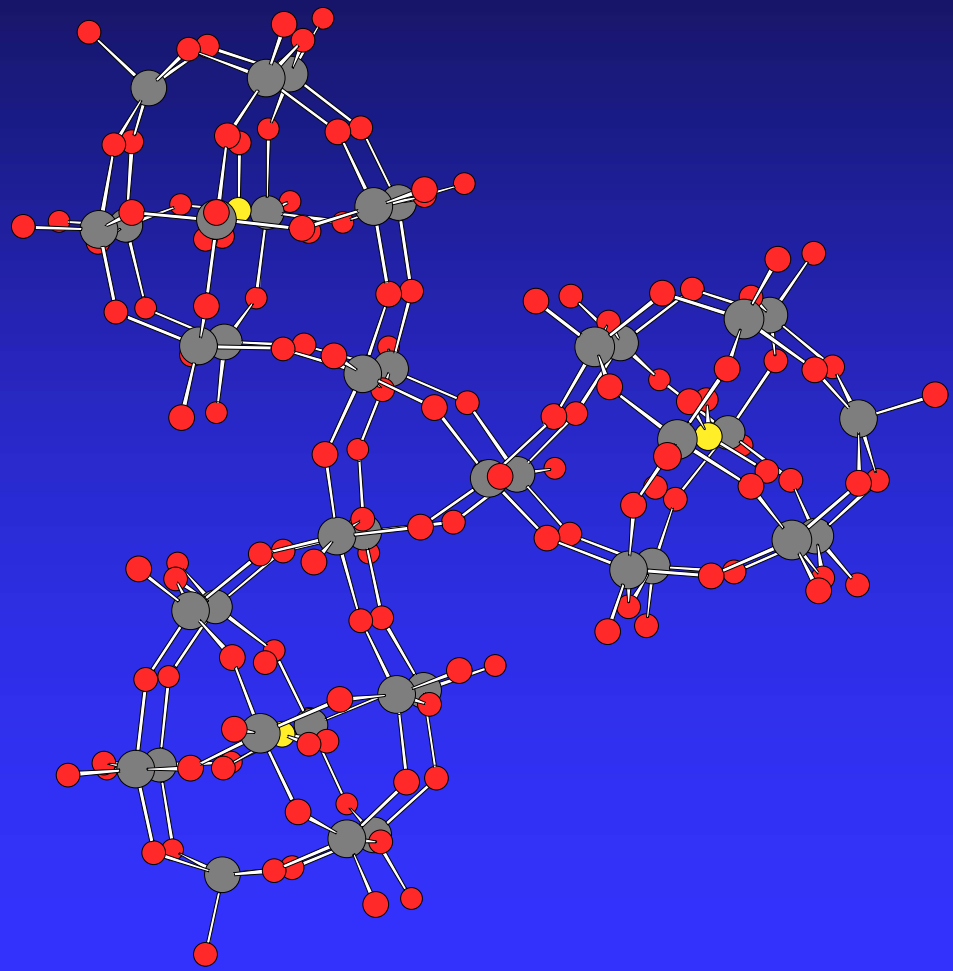
$[As_2W_{21}O_{69}]^{6-}$

(HAs2W)

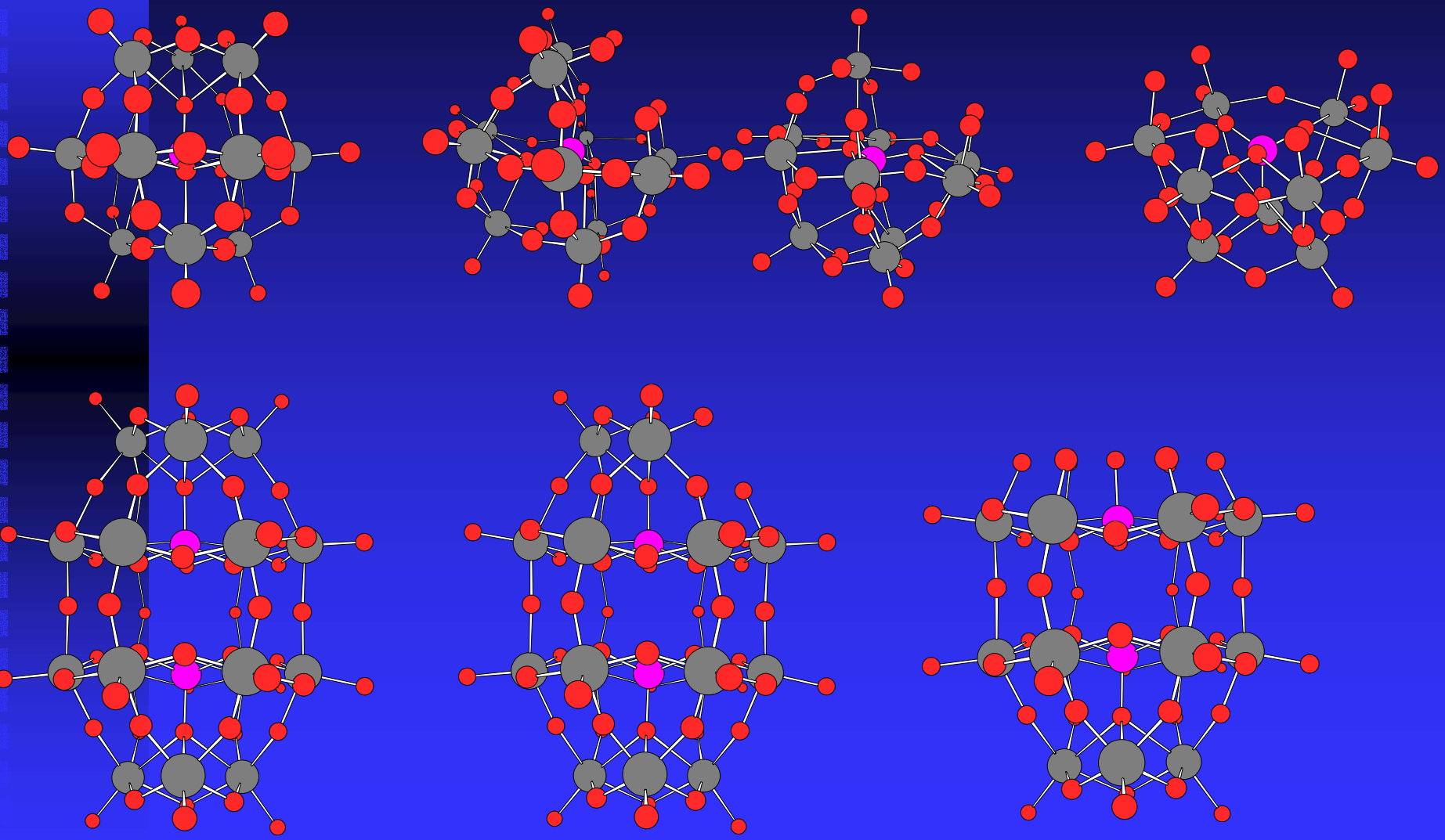
$[P_2W_{21}O_{71}]^{6-}$

(HP2W)

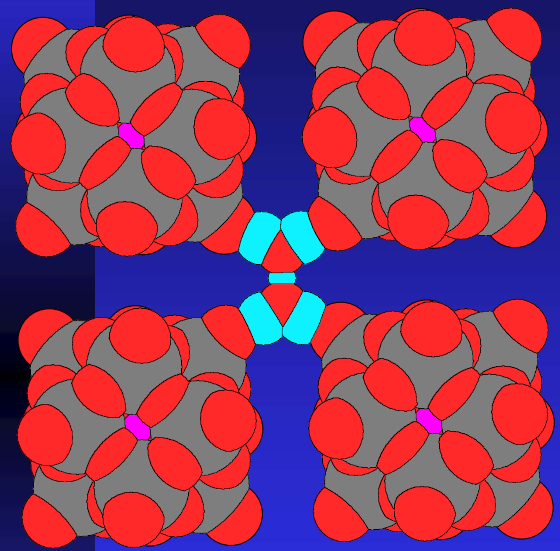
$[B_3W_{39}O_{132}]^{21-}$ - triflower



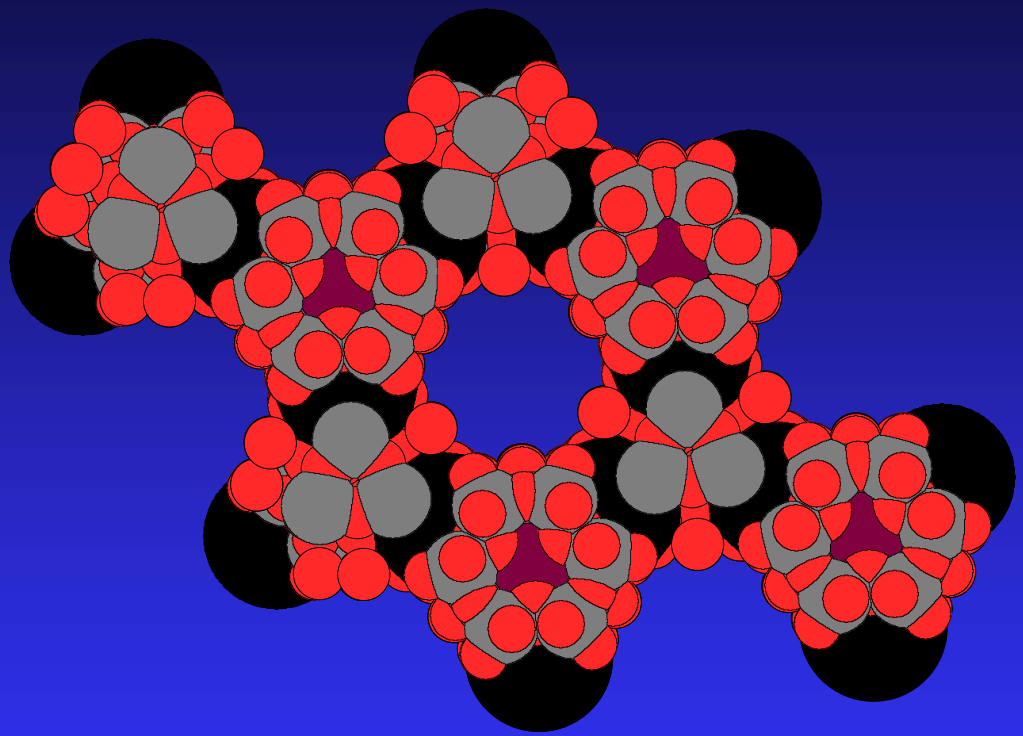
Lacunary Anions – Building Blocks



Secondary Structure Environments

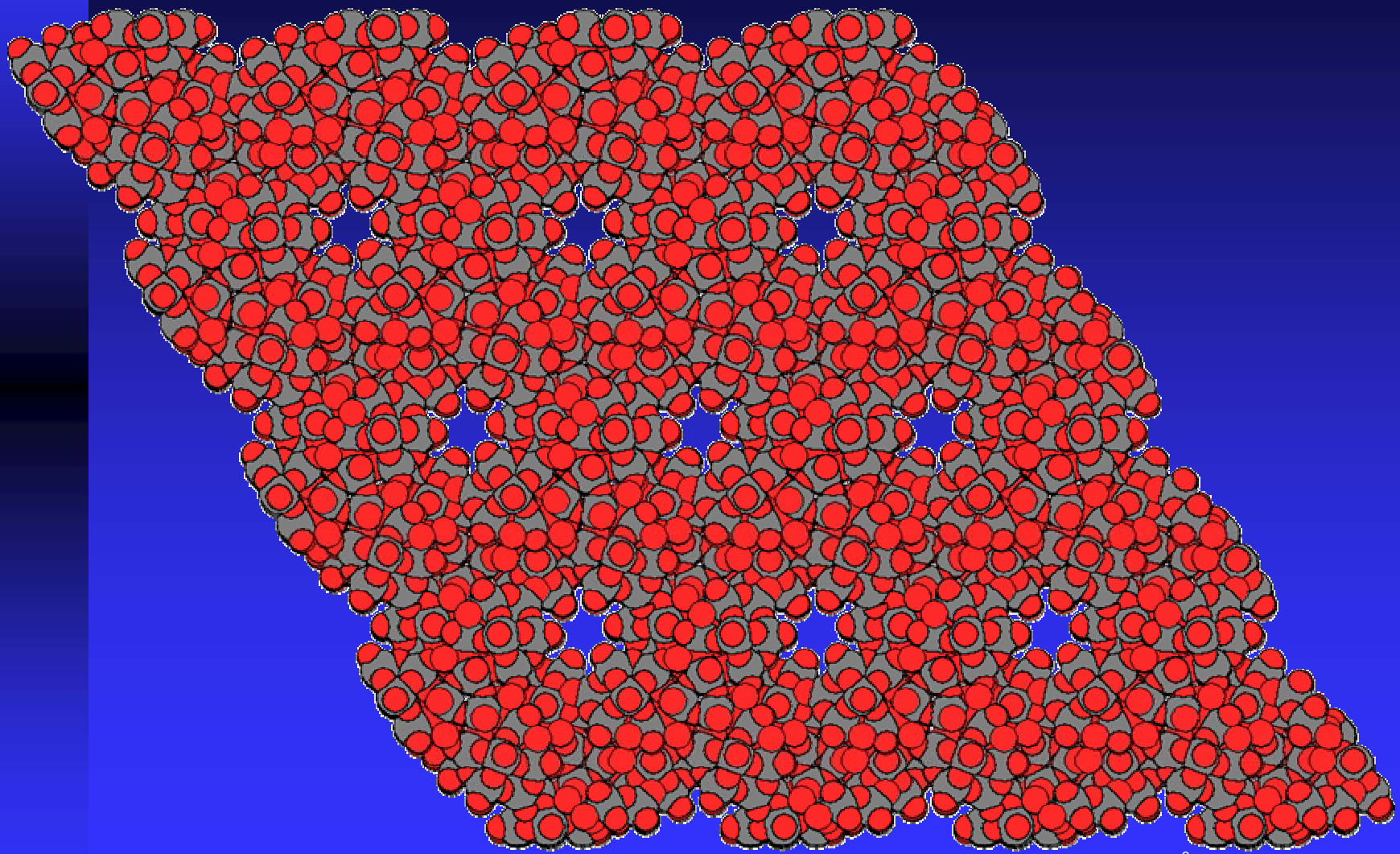


In $H_3PW_{12}O_{40}.6H_2O$
base centered cubic arranged
cavities contain $H_5O_2^+$
cations



In $H_2Rb_4As_2W_{21}O_{69}.35H_2O$
large channels, radius 4 Å,
along the z axis of the crystal
contain half the water
molecules in a disordered array

$H_{21}B_3W_{39}O_{132}$



Channel size: O…O distance in each TRIANGLE (Note: not hexagon) 5.450 Å

Synthesis

$SiO_3^{2-} + WO_4^{2-} \xrightarrow[\text{Acidic}]{} [\alpha\text{-}SiW_{12}O_{40}]^{4-} \xrightarrow[\text{pH 5-6}]{} [\alpha\text{-}SiW_{11}O_{39}]^{8-} \xrightarrow[\text{Basic}]{} [\alpha\text{-}SiW_9O_{34}]^{10-}$

$[\alpha\text{-}PW_{11}O_{39}]^{7-} \xrightarrow[\text{pH <5}]{} [\alpha\text{-}P_2W_{21}O_{71}]^{6-}$

$As_2O_3 + WO_4^{2-} \xrightarrow[\text{Acidic}]{} [As_2W_{21}O_{69}]^{6-}$

$H_3PO_4 + WO_4^{2-} \xrightarrow[\text{Acidic}]{} [\alpha\text{-}P_2W_{18}O_{62}]^{6-} \xrightarrow[\text{Basic}]{} [\alpha\text{-}P_2W_{17}O_{61}]^{10-} \xrightarrow{\text{Basic}} [\alpha\text{-}P_2W_{15}O_{56}]^{12-}$

Control of Protonation

- Free Acid Synthesis via Ion-exchange
  - Useful for incomplete acidification or preparation of anions that might be unstable under very acidic conditions
- Free Acid Synthesis via ether adduct extraction
  - Only fully acidified material extracted

Solubility

- Free Acids are water Soluble
- Addition of cations to free acid
  - Rarely form stoichiometric salt H-bonding determines stable species precipitated or formed
  - Associate with anchor material
  - Synthesize hybrid material

Redox

- Hydrogen
  - Reducible by H_2
    facile in heteropolymolybdates
  - Inter-electron transfer can be made slow
  - Reduction potential shifted by hydration
  - Use HPA redox to make water in membrane internally

Peroxide

- Hydrogen Peroxide
  - H_2O_2/HPA systems used as epoxidation catalysts
  - 12-Phosphotungstic Acid forms new oxygenated structures
  - Silicotungstic Acids stable H_2O_2
  - In practice not observed in PEM?
  - Develop HPA to decompose $^{\bullet}OH$?

Thermal Stability

- Ambient conditions – Large amount of water of crystallization

  ↓ 100°C

- Strongly bound secondary structure water

  ↓ 200°C

- Deprotonation – anhydrous protons leave with skeletal oxygen to give neutral HPA

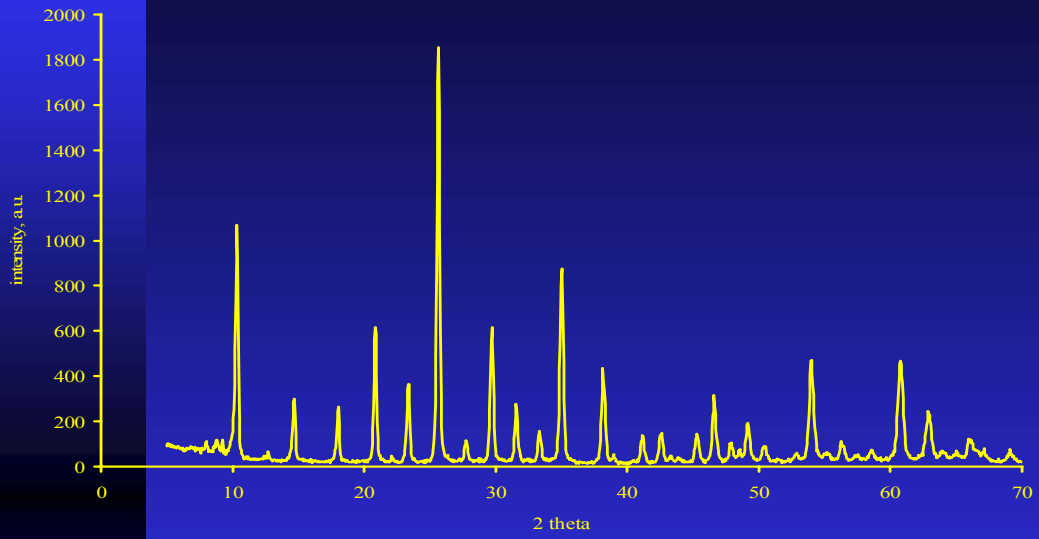
  ↓ >250°C

- Decomposition of Neutral HPA

TGA for HPA pretreated at 110 °C

HPA	Water of crystallization		Secondary structure water		Neutralization		Decomp.
	Equiv. H_2O	Temp.° C	Equiv. H_2O	Temp. °C	Equiv. H_2O	Temp. °C	Temp.° C
$H_3PW_{12}O_{40}$	1	50	6	164	1	482	589
$H_8SiW_{11}O_{38}$	2	60	7	152	6	410	611
$H_6SiV_2W_{10}O_{40}$			6	129	2	250	471
			2	250			
$H_8SiV_3W_{10}O_{40}$			7	183			477
$H_6P_2W_{18}O_{62}$			4	114	3	290	>600
$Na_xH_yP_2W_{18}O_{62}$	7	60	5	114			597
$H_6As_2W_{21}O_{69}$			12	129	4	430	430
			2	316			
$H_{21}B_3W_{39}O_{132}$	17	59	7	203	4	358	405

Oven dried Keggin produce cubic structures



$Na2HPW12O40.6H_2O$

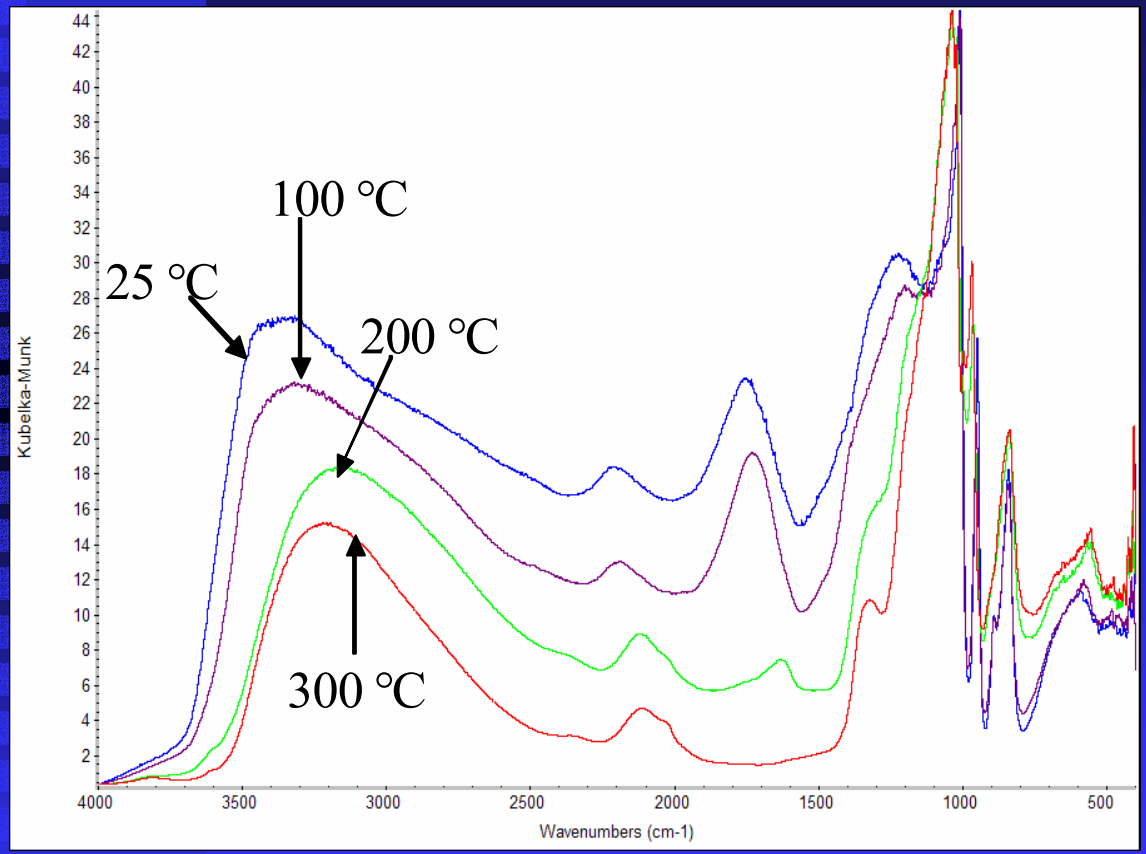
Cation	Number of Protons	Ionic radius, Å	Lattice parameter, a, Å
H	3		12.01
Na	1	0.97	11.95
K	<0.5	1.33	11.59
Cs	0.5	1.67	11.81

Volume of lattice dependant on residual number of protons.
Note that the cesium salt is totally insoluble in water or dilute acid.

Infrared Spectroscopy

- 3800 – 2000 cm^{-1} υ(OH)
  - Empirical bond length correlation
  - Well established H-bond energy relationship
- 2000 – 1200 cm^{-1} δ(OH)
  - 1750 cm^{-1} $H_5O_2^+$
  - 1650 cm^{-1} H_3O^+
- 1200 – 800 cm^{-1}
  - anion bands:υ(XO), υ(W=O_t), υ(WO_e), υ(WO_c)
- <800 cm-1 γ(OH)

DRIFTS spectra of $H_8SiW_{11}O_{39}$

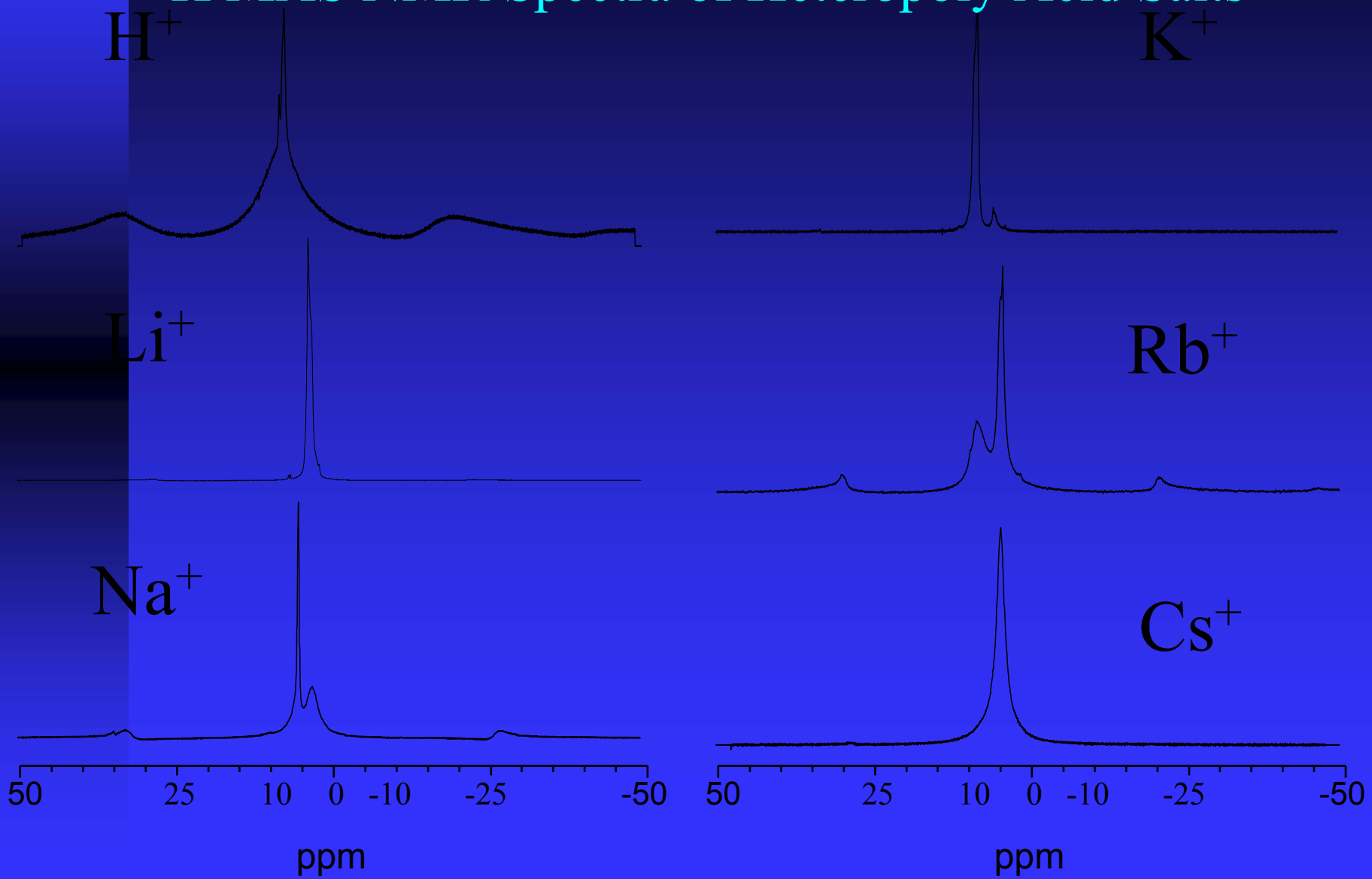


- <200°C $H_5O_2^+$
- 200°C H_3O+
- >300°C OH strongly H-bound

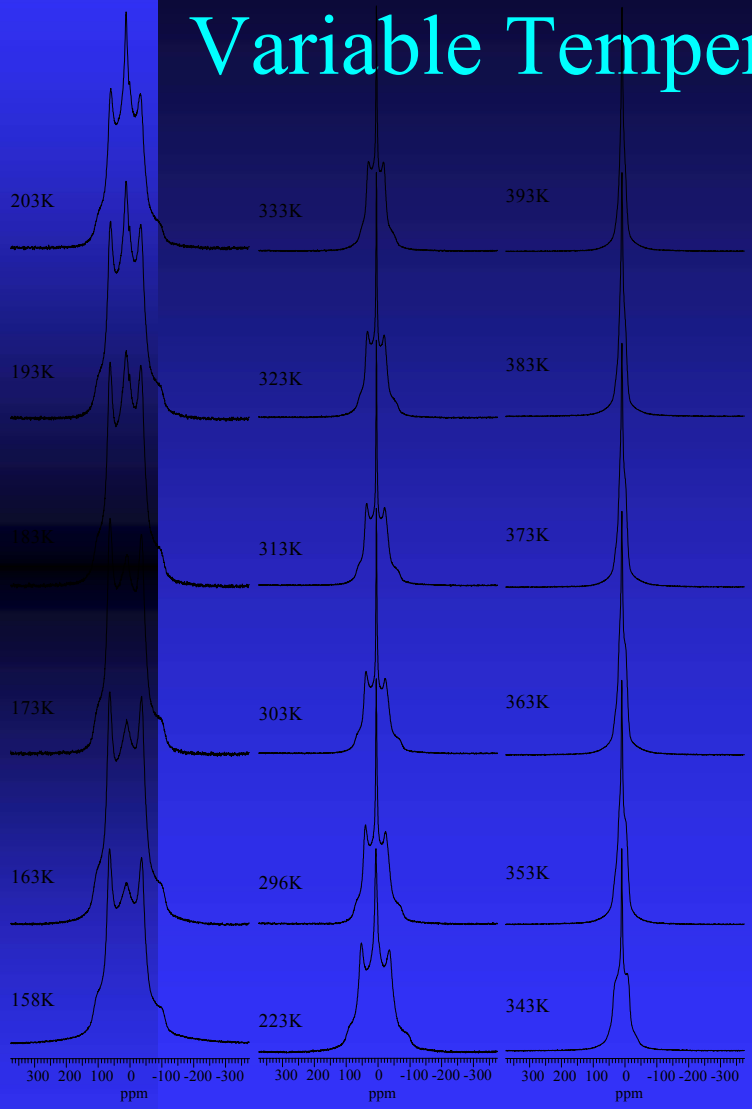
NMR

- ^{1}H, Magic angle spinning, MAS, used to determine chemical shifts (number and chemical environment of protons)
- ^{n}X, MAS, other nuclei used for structural analysis
- Non-spinning experiments give powder patterns in favorable cases, distances between like nuclei
- SEDOR/REDOR used to determine inter-atomic relations/distances between unlike nuclei
- T^{1}, T^{2} measurements used to probe structure

^{1}H MAS NMR Spectra of Heteropoly Acid Salts

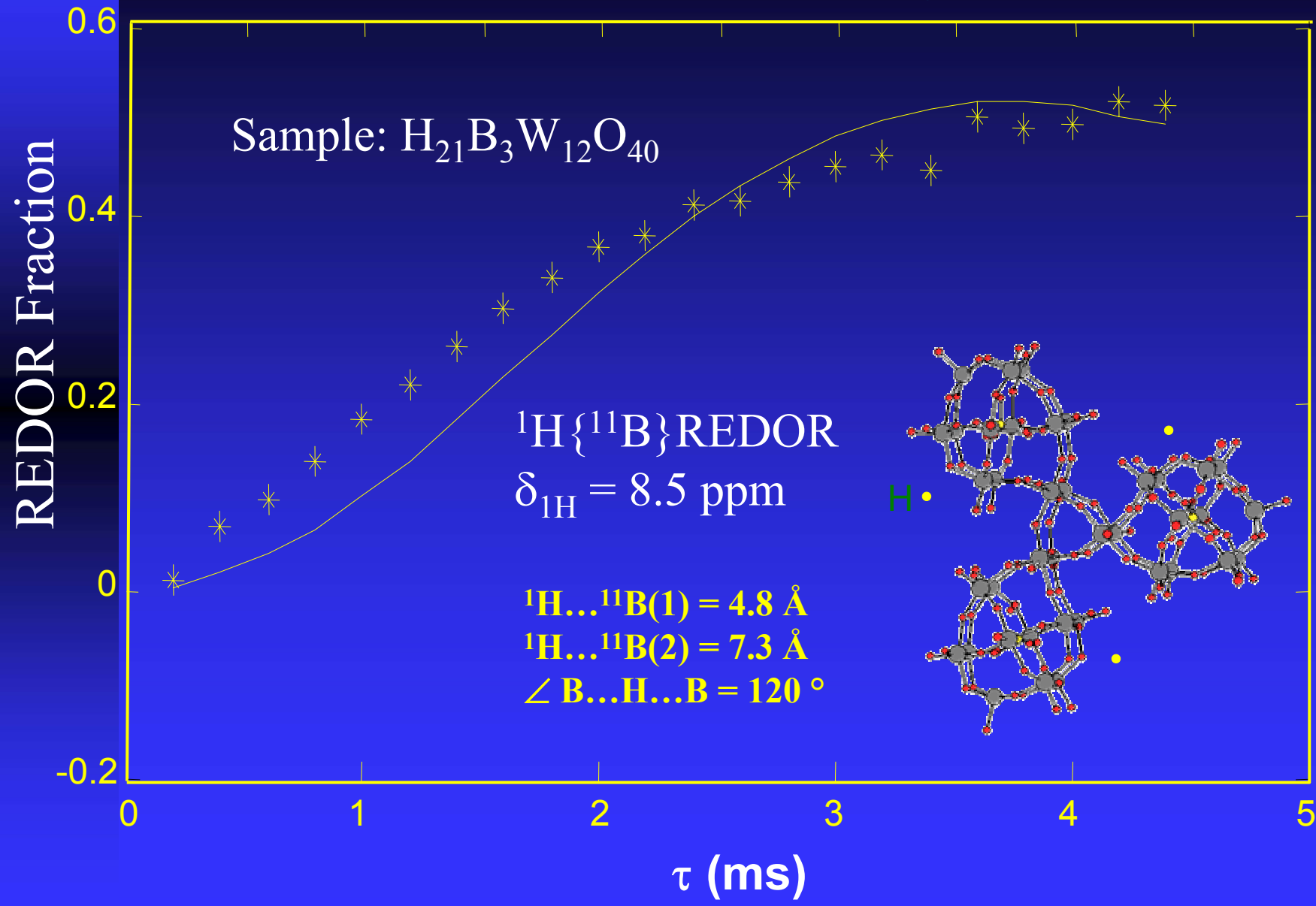


Variable Temperature NMR



- HNa2PW exhibits a powder pattern(non-spinning) which is indicative of an ordering of the protons in the structure
- Simulation of this pattern allows us to determine an interprotonic distance of 0.1596 nm
- As the pattern collapses at higher temperatures we can also deduce a diffusion coefficient of $1x10^{-4}$ cm^2 cm^{-1} at 393 K

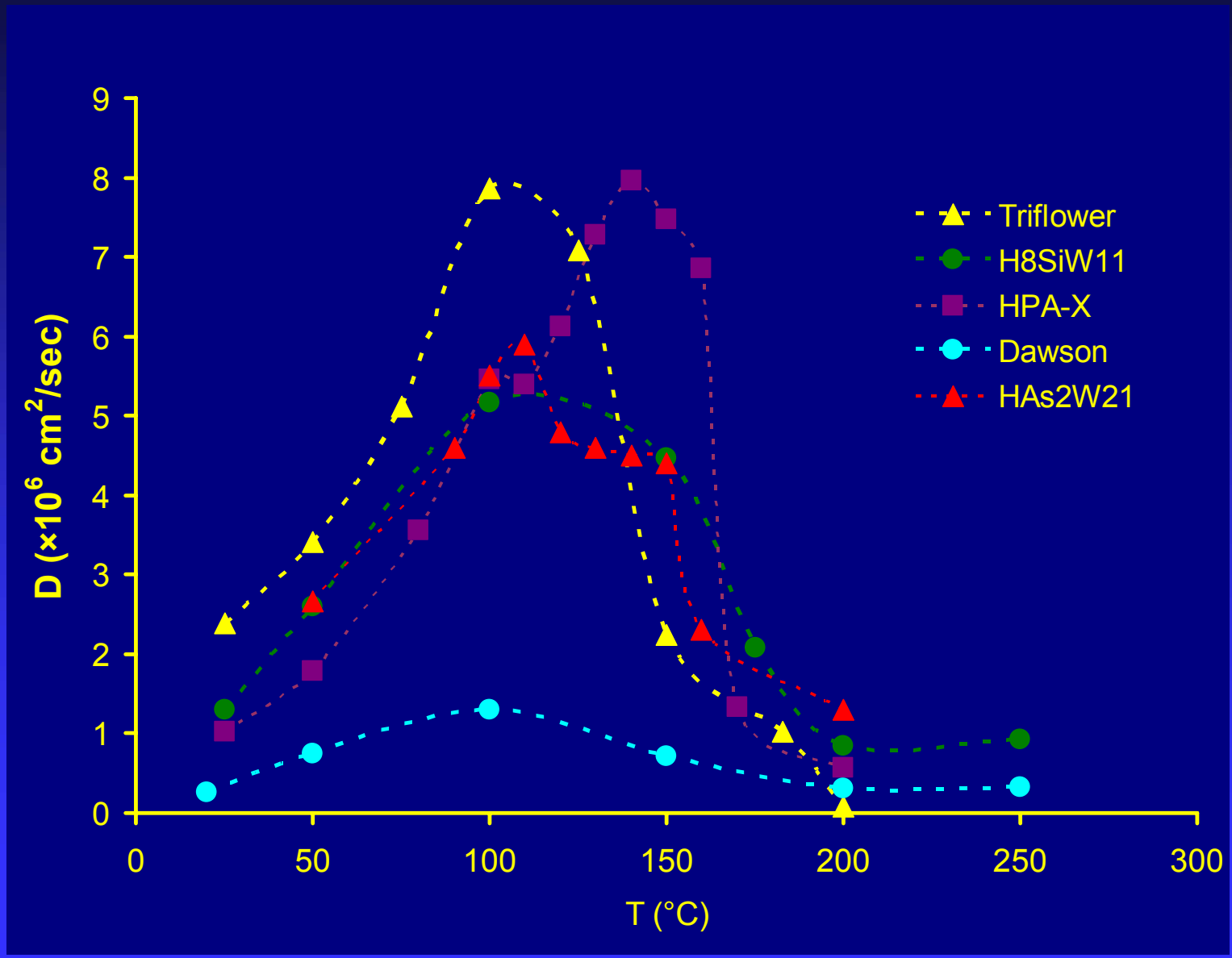
REDOR Modeling*



Proton Diffusion by PFGSE

- Proton diffusion coefficients can be unambiguously measured by pulse field gradient spin echo, PFGSE.
- A PFGSE probe with capability to 300°C was commissioned from Doty Scientific from funds awarded by the NSF
- For the correct operation of the variable temperature, VT, features of this probe a DOTY, VT, controller was eventually purchased.
- The ability to measure proton diffusion coefficients to these elevated temperatures is unique to the CSM/NREL group.

Temp. dependent Diffusion Coefficients



Acknowledgements

- US DOE Science Initiative
- NREL

John Turner

Steven F. Dec

Danielle Hansgen

Jim Horan

Jennifer L. Malers

Fanqin Meng

Jimmy O'Dea

John Pern

Mary Ann Sweikart

David Vernon